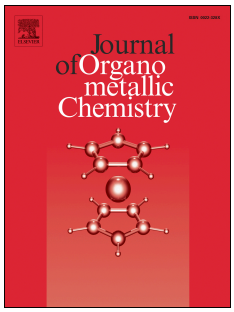
Accepted Manuscript



Platinum(II) complexes of some unsymmetrical diphosphenes

Keith B. Dillon, Mark A. Fox, Vernon C. Gibson, Helen P. Goodwin, Leila J. Sequeira

PII: S0022-328X(16)30443-0

DOI: 10.1016/j.jorganchem.2016.10.005

Reference: JOM 19649

To appear in: *Journal of Organometallic Chemistry*

Received Date: 18 August 2016

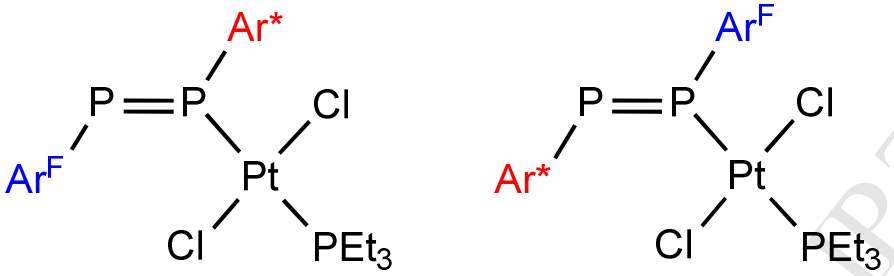
Revised Date: 29 September 2016

Accepted Date: 2 October 2016

Please cite this article as: K.B. Dillon, M.A. Fox, V.C. Gibson, H.P. Goodwin, L.J. Sequeira, Platinum(II) complexes of some unsymmetrical diphosphenes, *Journal of Organometallic Chemistry* (2016), doi: 10.1016/j.jorganchem.2016.10.005.

Graphical Abstract

Configurations of new platinum(II) complexes with unsymmetrical diphosphenes were determined by a combination of observed and computed ^{31}P NMR data.



Ar* = 2,4,6-^{t}Bu$_3$C$_6$H$_2$

Ar^F = 2,4,6-(CF$_3$)$_3$C$_6$H$_2$

Platinum(II) Complexes of some Unsymmetrical Diphosphenes

Keith B. Dillon[*a], Mark A. Fox[*a], Vernon C. Gibson[b], Helen P. Goodwin[a] and Leila J. Sequeira[a]

[a] Chemistry Department, University of Durham, South Road, Durham DH1 3LE, UK

[b] Department of Chemistry, Imperial College London, Exhibition Road, London SW7 2AZ, UK

Abstract

Reaction of the unsymmetrical diphosphene Ar*P=PAr^F **1** (Ar* = 2,4,6-^{t}Bu$_3$C$_6$H$_2$, Ar^F = 2,4,6-(CF$_3$)$_3$C$_6$H$_2$) with the dimeric platinum(II) species *trans*-[Pt(PEt$_3$)Cl(μ-Cl)]$_2$ led initially to the formation of two different monomeric Pt(II) complexes *trans*-[Pt(PEt$_3$)Cl$_2$(Ar*P=PAr^F)] **2** and *trans*-[Pt(PEt$_3$)Cl$_2$(Ar^{F}P=PAr*)] **3**, where the underlined phosphorus atom coordinates to Pt. These were readily identifiable by ^{31}P NMR solution-state spectroscopy, but attempts to separate them by column chromatography were unsuccessful. When the reaction was repeated on a larger scale, a third complex *cis*-[Pt(PEt$_3$)Cl$_2$(Ar^{F}P=PAr*)] **4** was detected in solution, with P-Ar^F bound to Pt. Calculations of energies and ^{31}P NMR chemical shifts confirm that this species is expected to be the thermodynamically most stable monomeric reaction product. For comparison, we have also prepared the analogous Pt(II) complex *trans*-[Pt(PEt$_3$)Cl$_2$(Ar*P=PAr*)] **6** of the symmetrical diphosphene Ar*P=PAr* **5**, and obtained its ^{31}P NMR parameters in solution. The mixed diphosphene Ar'P=PAr^F **7** (Ar' = 2,6-(CF$_3$)$_2$C$_6$H$_3$) reacts with the same platinum(II) dimer to yield a single *cis*-complex **8**. Calculations have enabled us to assign the ^{31}P chemical shifts of this unsymmetrical diphosphene **7**, and to show that the Ar' group is coordinated to Pt in the unique product *cis*-[Pt(PEt$_3$)Cl$_2$(Ar'P=PAr^F)] **8**.

Introduction

Since the first diphosphene Ar*P=PAr* **5** (Ar* = 2,4,6-^{t}Bu$_3$C$_6$H$_2$) was prepared by Yoshifuji and co-workers in 1981, [1] a great deal of interest has focused on their coordination chemistry. [2,3] They can bind to transition metal fragments either in an η^1 fashion, via a lone pair on phosphorus, or in an η^2 mode, utilising the π system of the P=P double bond; some examples of both coordination types for Ar^{F}P=PAr^F **9** (Ar^F = 2,4,6-(CF$_3$)$_3$C$_6$H$_2$), [4] with strongly electron-withdrawing substituents, have been reported by us. [5,6] Occasionally it is possible to coordinate a metal to each of the phosphorus atoms in an η^1 mode, as in the mono- and di-AuCl complexes of Ar*P=PAr* **5** (Ar* = 2,4,6-^{t}Bu$_3$C$_6$H$_2$). [7] For an unsymmetrical diphosphene R^{1}P=PR^2 there is the additional possibility of η^1 coordination by either of the inequivalent phosphorus atoms. Cowley *et al*. showed that the diphosphene 2,4,6-^{t}Bu$_3$C$_6$H$_2$P(1)=P(2)CH(SiMe$_3$)$_2$ reacted with Fe$_2$(CO)$_9$ to afford a single product in 63% yield, with Fe(CO)$_4$ coordinated to P(2). [8] This observation is consistent with

coordination by the less sterically hindered phosphorus atom, but was not discussed further. Yoshifuji and co-workers have prepared $M(CO)_5$ complexes (M = Cr, Mo or W) of the unsymmetrical diphosphene Ar*P=PMes (Mes = 2,4,6-$Me_3C_6H_2$ or mesityl), and have shown that these can be photoisomerised from the *E*- to the *Z*-isomer. [9] In these complexes the metal was again coordinated to the less sterically hindered phosphorus atom. More recent studies on unsymmetrical diphosphenes, usually with a phosphorus-containing substituent on one of the diphosphene phosphorus atoms, and some metal complexes thereof, have also appeared in the literature. [10-14]

We have described the transition metal-catalysed metathesis of phosphorus – phosphorus double bonds, in which symmetrical or unsymmetrical diphosphenes can be synthesised from appropriate dichlorophosphanes by interaction with $W(PMe_3)_6$, as shown in equation (1) for an unsymmetrical species. [15]

$$RPCl_2 + R'PCl_2 + W(PMe_3)_6 \rightarrow RP{=}PR' + 3\ PMe_3 + WCl_4(PMe_3)_3 \qquad (1)$$

It is also possible to synthesise unsymmetrical diphosphenes by base-catalysed elimination in one of two ways, equations (2) and (3). [2]

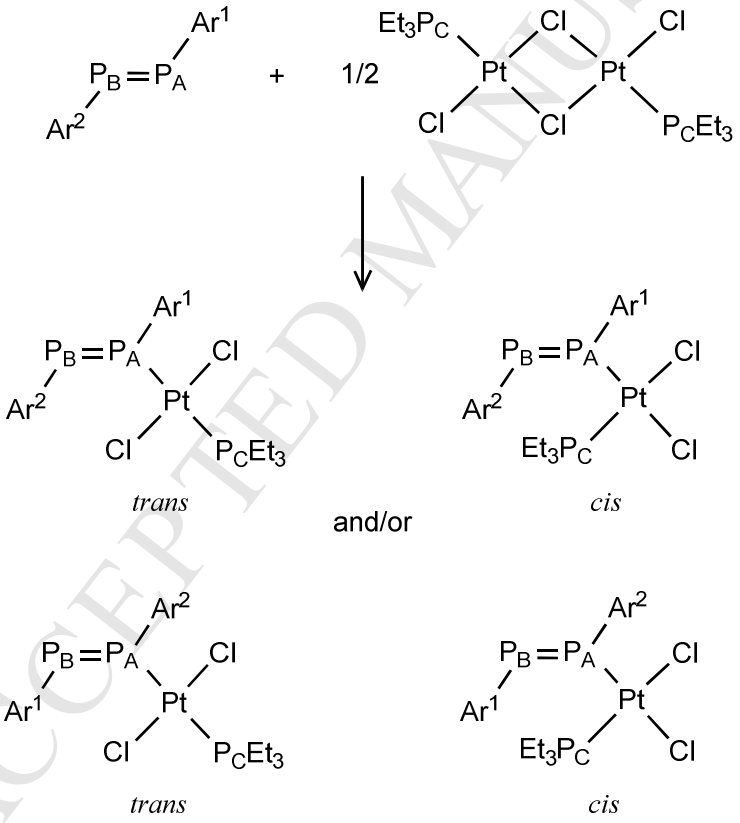
$$RPH_2 + R'PX_2 + 2\ DBU \rightarrow RP{=}PR' + 2\ DBUH^+\ X^- \qquad (2)$$

$$RPX_2 + R'PH_2 + 2\ DBU \rightarrow RP{=}PR' + 2\ DBUH^+\ X^- \qquad (3)$$

(DBU = 1,8-diazabicyclo[5,4,0]undec-7-ene)

It was therefore of considerable interest to investigate the behaviour of other unsymmetrical diphosphenes towards a suitable transition metal moiety. We have synthesised the unsymmetrical diphosphenes $Ar^*P{=}PAr^F$ **1** (Ar^* = 2,4,6-$^tBu_3C_6H_2$, Ar^F = 2,4,6-$(CF_3)_3C_6H_2$) via the route shown in equation (1), and the species $Ar'P{=}PAr^F$ **7** (Ar' = 2,6-$(CF_3)_2C_6H_3$) by both pathways shown in equations (2) and (3). These compounds have been fully characterised. The unsymmetrical products have then been reacted in a 2 : 1 molar ratio with the dimeric platinum(II) compound *trans*-$[Pt(PEt_3)Cl(\mu\text{-}Cl)]_2$, to investigate whether steric or electronic effects dominate possible complex formation (Scheme 1). While ^{31}P NMR solution-state spectroscopy

has been the main experimental means of following these reactions, calculations have also been carried out, to establish the most stable complexes from a thermodynamic viewpoint, and to calculate their chemical shifts. In addition to providing convincing support for the identification of the observed complexes in the $Ar^*P{=}PAr^F$ **1** reaction, this procedure has enabled the resonances to be assigned for $Ar'P{=}PAr^F$ **7**, and established the identity of the sole product **8** from this reaction. The behaviour of the platinum(II) dimer with the original Yoshifuji diphosphene $Ar^*P{=}PAr^*$ **5** has also been investigated for comparison purposes. We have previously reported that this dimer with symmetrical $Ar^FP{=}PAr^F$ **9** forms *cis*-$[PtCl_2(PEt_3)(Ar^FP{=}PAr^F)]$ **10** as the unique product with the diphosphene coordinated η^1 by one of the phosphorus atoms. [5]



Scheme 1. General synthesis of η^1-Pt(II) complexes from unsymmetrical diaryldiphosphenes.

Results and Discussion

(a) Reaction of *trans*-[Pt(PEt_3)Cl(μ-Cl)]$_2$ with Ar*P=PAr* **5**

A 1:2 stoichiometric mixture of the reagents in C_6D_6 was sealed into an NMR tube. After a few hours at room temperature, some of the starting material had been consumed, and new signals were apparent in the ^{31}P NMR spectrum. A doublet at 380 ppm ($^1J_{P_AP_B}$ 548 Hz) was readily assigned to the uncoordinated phosphorus in an η^1 diphosphene complex, while a doublet of doublets with platinum satellites was seen at 353 ppm ($^1J_{PtP_A}$ 2200 Hz, $^1J_{P_AP_B}$ 548 Hz, $^2J_{P_AP_C}$ 487 Hz). There was also a doublet signal for the PEt_3 group with platinum satellites at 10.4 ppm ($^1J_{Pt\text{-}P_C}$ 2917 Hz, $^2J_{P_A\text{-}P_C}$ 487 Hz). The magnitudes of both $^1J_{PtP}$ and $^2J_{P_AP_C}$ clearly denote the formation of a *trans*-complex **6**, [16] as shown in Figure 1. The NMR data for all new species, including the parent unsymmetrical diphosphenes **1** and **7**, are collected in Table 1.

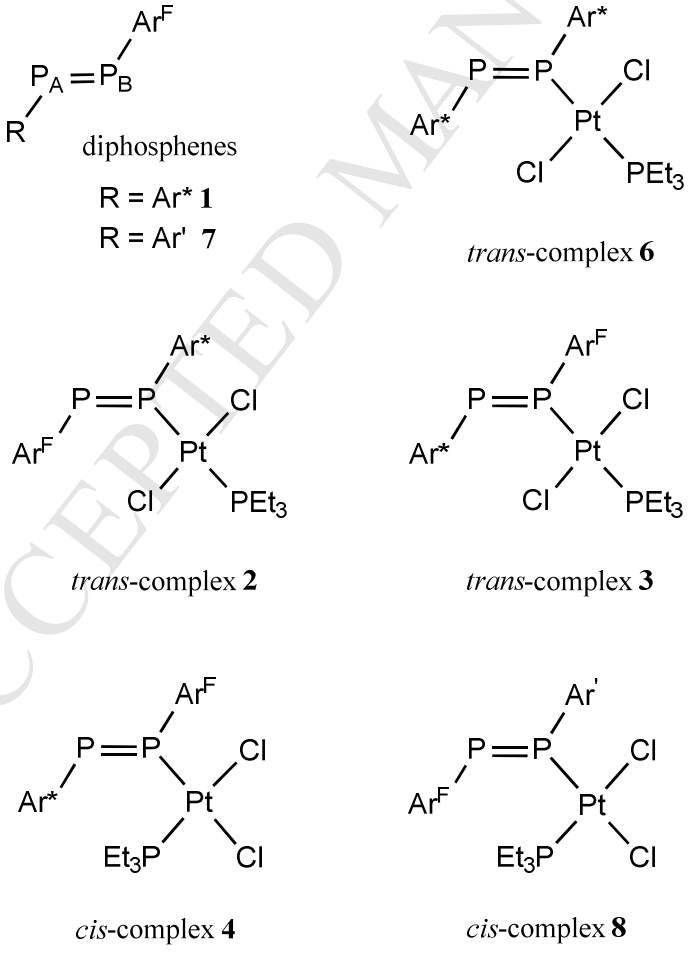


Figure 1. Compounds prepared in this study.

The large $^{2}J_{\mathrm{PA\text{-}PC}}$ values for *trans*-complexes **2**, **3** and **6** in Table 1 are entirely in keeping with previous work, and predictions from the literature. [17] For example, $^{2}J_{\mathrm{PP}}$ values between 469 and 598 Hz have been reported for nine different *trans*-complexes in three recent papers. [18-20]

Table 1. $^{31}P\{^{1}H\}$ NMR data (δ ^{31}P in ppm; *J* values in Hz); P_A = bound P in diphosphene for Pt complexes; P_B = 'free' P in diphosphene for Pt complexes; P_C = PEt_3; all RP=PR' forms are E.

Compound	Group at P_A	Group at P_B	δ P_A	δ P_B	$^{1}J_{P_AP_B}$	$^{1}J_{PtP_A}$	δ P_C	$^{1}J_{PtP_C}$	$^{2}J_{P_AP_C}$	*cis/trans* at Pt
1[a]	Ar*	Ar^F	536	417	570					
2	Ar*	Ar^F	400	308	529	2328	18.6	3000	528	*trans*
3	Ar^F	Ar^*	317	402	552	2406	19.2	3139	521	*trans*
4[b]	Ar^F	Ar^*	258	360	548	3735	9.6	3174		*cis*
5	Ar^*	Ar^*	494							
6	Ar^*	Ar^*	353	380	548	2200	10.4	2917	487	*trans*
7	Ar'	Ar^F	489	478	552					
8	Ar'	Ar^F	386	334	501	2550	NR[c]	NR[c]		*cis*
9 Ref. [5]	Ar^F	Ar^F	474							
10 Ref. [5]	Ar^F	Ar^F	347	337	534	2603	10	4024	-	*cis*

[a] $^{4}J_{P_BF}$ = 22 Hz; [b] $^{2}J_{P_BPt}$ = 343 Hz; [c] NR = Not Recorded.

(b) Reaction of *trans*-[Pt(PEt_3)Cl(μ-Cl)]$_2$ with Ar*P_A=P_BAr^F **1**

A similar reaction was carried out with the unsymmetrical diphosphene **1**; in this instance the mixture was warmed to 60°C for 1 h in the NMR tube. The $^{31}P\{^1H\}$ NMR spectrum confirmed the presence of a small amount of unreacted starting material, together with two new complexes **2** and **3** (Table 1). Analysis of the spectra was not trivial because of the close similarity between the values of $^1J_{P_AP_B}$ and $^2J_{P_AP_C}$, particularly for one of the compounds. The results clearly demonstrate, however, that both species have *trans* configurations, with either P_A(Ar*) **2** or P_A(Ar^F) **3** η^1-coordinated to Pt (Figure 1). The expected doublet for the uncoordinated P atom of the diphosphene ligand in each complex could be readily identified (Table 1). Signal intensities suggested a slight prevalence of complex **3** with P_A(Ar^F) bonded to Pt.

Attempts to separate these isomers by column chromatography were unsuccessful, as they decomposed during the process. When a scaled-up reaction was performed, ^{31}P NMR signals for a third complex **4** were detected; the latter gave a clean spectrum for *cis*-[$PtCl_2$(PEt_3)(Ar^FP_A=P_BAr*)], with P_A(Ar^F) coordinated to Pt (Figure 2), as confirmed by the higher $^1J_{PtP_A}$ than for the corresponding *trans*-isomer **3**, and the absence of any large ^2J coupling between P_A and P_C in the PEt_3 group (Table 1).

Since *cis* complexes are usually more stable than *trans*, **4** may well be the thermodynamic reaction product, suggesting that P(Ar^F) is a rather better donor than P(Ar*). A reasonable assumption is that **2** and **3** are initially formed in an equilibrium mixture from **1**; reaction was not complete, as shown by the presence of a small amount of starting material. As *trans*-isomer **3** converts to the thermodynamically more stable *cis*-isomer **4**, removal of **3** from the equilibrium will result in conversion of **2** to **3**. Eventually **4** will remain as the only product. This conclusion is fully supported by the calculations discussed below, which indicate that complex **4** is the most stable of all four possible single η^1-bonded species. Although the electronegative CF_3 groups in Ar^F would tend to reduce the effectiveness of donation from the phosphorus lone pair, electronic effects seem to be outweighed by the steric hindrance to complexation caused by the very bulky *ortho*-^{t}butyl groups in PAr*.

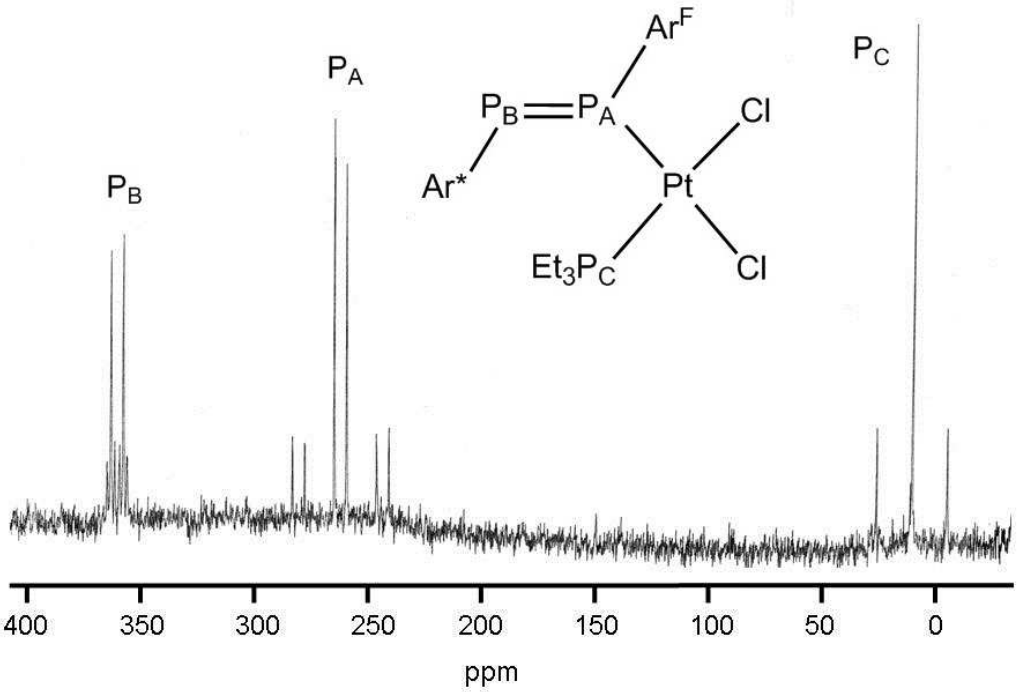


Figure 2. ^{31}P NMR spectrum for the *cis*-complex, [$PtCl_2(PEt_3)(Ar^FP{=}PAr^*)$], **4**.

There are two other points of particular interest in the $^{31}P\{^1H\}$ NMR spectrum of **4** (Figure 2 and Table 1). Firstly, the $^1J_{PtP_C}$ value (for the PEt_3 group) is smaller than usually observed in *cis*-complexes, although slightly larger than that in **3**. Secondly, $^2J_{PtP_B}$ coupling (to the PAr* group) is clearly apparent, with a coupling constant of 343 Hz; this behaviour was not observed in any of the other systems studied. These results may indicate a slightly unusual configuration for the coordinated diphosphene in **4**, bringing P_B somewhat closer to platinum than normal and forcing P_C further away.

(c) Reaction of $[Pt(PEt_3)Cl_2]_2$ with Ar'P=PAr^F **7**

A parallel reaction to those described above was carried out between the platinum dimer and Ar'P=PAr^F **7** at room temperature. The mixture was stirred for 1 h. $^{31}P\{^1H\}$ NMR spectroscopy revealed the presence of a single η^1-bonded *cis*-isomer **8** (Figure 1 and Table 1). This result was not unexpected, in view of the formation of a similar *cis*-complex **10** by the symmetrical diphosphene Ar^{F}P=PAr^F.[5] In itself the NMR spectrum of **8** did not allow the coordinating atom to be distinguished in the

unsymmetrical diphosphene, since similar ^{31}P spectra would result, irrespective of whether P(Ar') or P(Ar^F) was the donor atom. Calculations described below indicate that P(Ar') coordinates to Pt, and also enable the resonances to be assigned for the starting material **7**. In this system, comparable steric hindrance would be expected from both potential donor sites, because each phosphorus has two *ortho*-CF_3 groups. The Ar' moiety is expected to be rather less electronegative than Ar^F, however, hence a better donor, and this is entirely in keeping with the deductions above.

(d) Calculations

Geometries of known and new diaryldiphosphenes were optimised at B3LYP/6-31G*, to assess the accuracy of the computations by comparing with reported X-ray data [21-23] where available, and by comparing computed ^{31}P GIAO-NMR data on the optimised geometries with observed ^{31}P NMR shifts, which are summarised in Table 2. The calculated P=P bond lengths are consistently longer by 0.02 Å, whereas the agreement between computed and observed ^{31}P NMR data [24] is good. The more computationally intensive model chemistries B3LYP/6-311G** and B3LYP/cc-pVDZ gave geometric data no better than B3LYP/6-31G* (Table S1) thus B3LYP/6-31G* is used here. For the new diphosphene **7**, the ^{31}P peaks may thus be assigned with confidence. Similar computations were also carried out for known diphosphenes coordinated to cationic methyl group [25] or metals in an η^1 fashion [7,9,26] as listed in Table 2, and Figure 3 demonstrates the good agreement between observed and computed (GIAO) ^{31}P NMR data.

Table 2. Comparison of computed (B3LYP/6-31G*//GIAO-NMR) and observed P=P bond lengths (in Å) and ^{31}P chemical shifts (δ ^{31}P in ppm) for known diaryl diphosphenes $Ar^1P_A=P_BAr^2$, $[Ar^1(Me)P_A=P_BAr^2]^+$ cation and complexes of type $Ar^1\{R\}P_A=P_BAr^2$.

Ar^1	Ar^2	R	P=P E/Z		P=P (calc)	P=P (obs)	Reference	δ P_A (calc)	δ P_A (obs)	δ P_B (calc)	δ P_B (obs)	Reference
Ar^F	Ar*	-	E	**1**	2.052			400.5	*417.0*	536.7	*536.0*	This work
Ar*	Ar*	-	E	**5**	2.062	*2.034(2)*	[21]	487.9	*492.4*			This work
Ar'	Ar^F	-	E	**7**	2.040			479.1	*489.0*	466.8	*478.0*	This work
Ar^F	Ar^F	-	E	**9**	2.040	*2.022(2)*	[22]	467.9	*473.9*			This work
Ar'	Ar'	-	E		2.040	*2.019(2)*	[23]	477.5	*477.0*			[24]
Ar'	Ar*	-	E		2.051			408.7	*422.1*	535.1	*533.0*	[24]
Ar*	Ar*	$-Me^+$	E		2.046	*2.024(2)*	[25]	349.1	*332.2*	216.8	*237.0*	[25]
Ar'	Ar'	$-Cr(CO)_5$	E		2.043			439.5	*431.0*	440.5	*432.6*	[26]
Ar^F	Ar^F	$-Cr(CO)_5$	E		2.046			437.8	*430.2*	437.4	*427.6*	[26]
Mes	Ar*	$-Cr(CO)_5$	E		2.052			415.8	*412.3*	527.0	*500.9*	[9]
Mes	Ar*	$-Cr(CO)_5$	Z		2.055	*2.039(3)*	[9]	374.5	*384.9*	408.3	*393.9*	[9]
Ar*	Ar*	-AuCl	E		2.051	*1.975(5)*	[7]	320.1	*339.0*	395.5	*386.0*	[7]

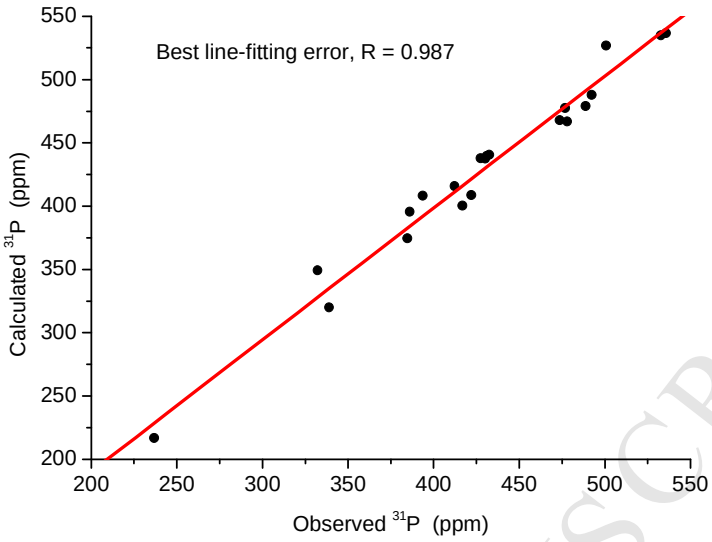


Figure 3. Comparison between computed and observed ^{31}P chemical shifts for diaryl diphosphenes and related derivatives listed in Table 2.

The platinum complexes observed experimentally are more complicated computationally, as there are many possible conformers and orientations. For simplification and reduced computational times, PMe_3 was used instead of PEt_3 in the model geometries **11**-**22** where all possible isomers were investigated at B3LYP/LANL2DZ:6-31G*. Table 3 compares the computed ^{31}P GIAO-NMR data for **11**-**22** with observed complexes **2**-**4**, **6**, **8** and **10**. The agreement with observed complexes is less precise, but all observed data fit best with the data of the expected isomer out of the possible structures. The relative energies between the model isomers **11**-**22** are listed in Table 4. The most stable isomers computationally are all found experimentally i.e. **13**, **16**, **17** and **21** for **4**, **6**, **8** and **10** respectively. The less thermodynamically stable isomers **2** and **3** observed are the next two most stable forms computationally, whereas the *cis*-isomer with the Ar* group at P_A is unfavourable due to sterics, as shown pictorially in Figure 4.

Table 3. Computed ^{31}P chemical shifts (δ ^{31}P in ppm) for η^1-coordinating diphosphene-platinum complexes [$PtCl_2(P_CR_3)(R^1P_A{=}P_BR^2)$]. P_A = bound P in diphosphene; P_B = 'free' P in diphosphene; P_C = PMe_3 or PEt_3; All $R^1P{=}PR^2$ forms are E. Observed data of reported compounds are included in italics for comparison.

Compound		δ P_A	δ P_B	δ P_C	Compound		δ P_A	δ P_B	δ P_C
cis-[$PtCl_2(PMe_3)(Ar^*P{=}PAr^F)$]	**11**	344.8	285.2	5.1	*trans*-[$PtCl_2(PMe_3)(Ar^*P{=}PAr^F)$]	**12**	407.2	314.0	7.0
					trans-[$PtCl_2(PEt_3)(Ar^*P{=}PAr^F)$]	**2**	*400*	*308*	*21*
cis-[$PtCl_2(PMe_3)(Ar^FP{=}PAr^*)$]	**13**	285.2	384.1	10.4	*trans*-[$PtCl_2(PMe_3)(Ar^FP{=}PAr^*)$]	**14**	318.1	417.1	8.2
cis-[$PtCl_2(PEt_3)(Ar^FP{=}PAr^*)$]	**4**	*258*	*360*	*10*	*trans*-[$PtCl_2(PEt_3)(Ar^FP{=}PAr^*)$]	**3**	*317*	*402*	*19*
cis-[$PtCl_2(PMe_3)(Ar^*P{=}PAr^*)$]	**15**	317.5	372.0	4.4	*trans*-[$PtCl_2(PMe_3)(Ar^*P{=}PAr^*)$]	**16**	374.9	391.2	3.4
					trans-[$PtCl_2(PEt_3)(Ar^*P{=}PAr^*)$]	**6**	*353*	*380*	*10*
cis-[$PtCl_2(PMe_3)(Ar'P{=}PAr^F)$]	**17**	342.0	315.4	10.3	*trans*-[$PtCl_2(PMe_3)(Ar'P{=}PAr^F)$]	**18**	382.1	345.4	6.6
cis-[$PtCl_2(PEt_3)(Ar'P{=}PAr^F)$]	**8**	*386*	*334*	*NR*					
cis-[$PtCl_2(PMe_3)(Ar^FP{=}PAr')$]	**19**	329.3	326.4	11.8	*trans*-[$PtCl_2(PMe_3)(Ar^FP{=}PAr')$]	**20**	371.6	364.2	6.7
cis-[$PtCl_2(PMe_3)(Ar^FP{=}PAr^F)$]	**21**	336.1	327.2	9.9	*trans*-[$PtCl_2(PMe_3)(Ar^FP{=}PAr^F)$]	**22**	374.9	352.8	8.0
cis-[$PtCl_2(PEt_3)(Ar^FP{=}PAr^F)$]	**10**	*347*	*337*	*10*					

Table 4. Relative energies in kcal mol^{-1} for *cis*- and *trans*- isomers of model platinum complexes, **11**-**22**. P_A = bound P in diphosphene. All ArP=PAr forms are E. The observed complexes **2**-**4**, **6**, **8** and **10** are assigned to the corresponding model isomer.

Compound	Group at P_A	*cis*	*trans*	Group at P_A	*cis*	*trans*
$[PtCl_2(PMe_3)(Ar^*P{=}PAr^F)]$	Ar*	**11**	**12**	Ar^F	**13**	**14**
		4.4	3.8		0.0	3.4
$[PtCl_2(PEt_3)(Ar^*P{=}PAr^F)]$	Ar*		**2**	Ar^F	**4**	**3**
$[PtCl_2(PMe_3)(Ar^*P{=}PAr^*)]$	Ar*	**15**	**16**			
		0.4	0.0			
$[PtCl_2(PEt_3)(Ar^*P{=}PAr^*)]$	Ar*		**6**			
$[PtCl_2(PMe_3)(Ar'P{=}PAr^F)]$	Ar'	**17**	**18**	Ar^F	**19**	**20**
		0.0	1.8		0.1	2.2
$[PtCl_2(PEt_3)(Ar'P{=}PAr^F)]$	Ar'	**8**		Ar^F		
$[PtCl_2(PMe_3)(Ar^FP{=}PAr^F)]$	Ar^F	**21**	**22**			
		0.0	1.3			
$[PtCl_2(PEt_3)(Ar^FP{=}PAr^F)]$	Ar^F	**10**				

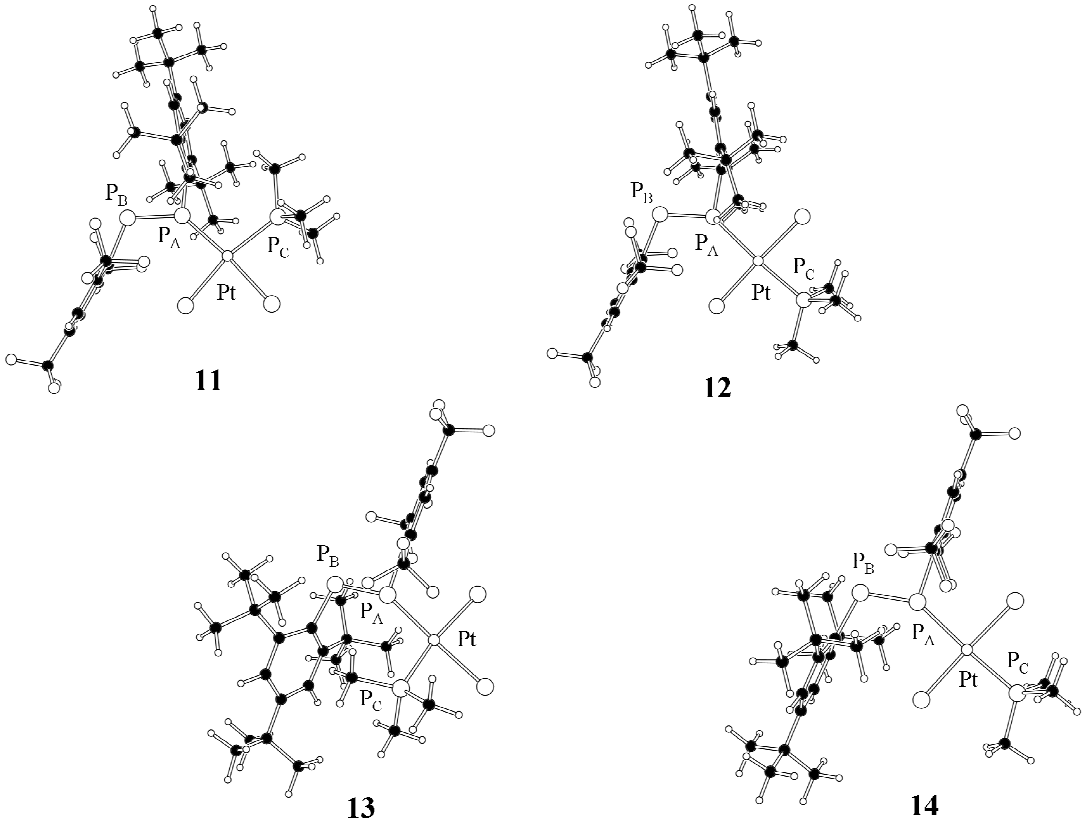


Figure 4. Optimised geometries of the model platinum complex, $[PtCl_2(PMe_3)(Ar^*P{=}PAr^F)]$, **11**-**14**.

Conclusions

Symmetrical diphosphene Ar*P=PAr* **5** forms a *trans*-complex **6** with *trans*-$[Pt(PEt_3)Cl(\mu\text{-}Cl)]_2$, whereas the unsymmetrical diphosphene Ar^FP=PAr' **7** yields a *cis*-complex **8**, parallel to the behaviour of $Ar^FP=PAr^F$, [5] with the PAr' group bonded to platinum, as shown by theoretical calculations. The most interesting results were obtained with the unsymmetrical diphosphene Ar*P=PAr^F **1**. Initially a mixture of two *trans*-complexes was formed, corresponding to separate η^1 coordination of Ar^FP **3** and Ar*P **2**, possibly with a slight preference for **3**. Subsequently a single *cis*-complex **4** was detected, with Ar^FP coordinated to Pt. Calculations confirm that this complex is expected to be the most thermodynamically stable of the four possible products with η^1 coordination. The results illustrate well the interplay of steric and electronic effects in complexes of unsymmetrical diphosphenes. The most sterically demanding group studied is Ar*, so that for Ar*P=PAr^F the least stable complex is calculated to be the one where the Ar*P group would be *cis* to the PEt_3 ligand on Pt. This is in full agreement with the experimental observations, even though Ar*P should be a better donor than Ar^FP. For Ar'P=PAr^F, where the steric effects should be similar for both potential donor sites, electronic effects take over, and coordination is observed only via the Ar'P group, which should be the better donor. Again theory and experiment are in agreement. The present work illustrates the value of combining experimental and theoretical studies of such systems.

Experimental

All manipulations, including the preparation of NMR samples, were carried out under an inert atmosphere of dry nitrogen, either using standard Schlenk and cannula techniques, or in a nitrogen-filled glovebox. Solvents were refluxed over an appropriate drying agent, and distilled and degassed prior to use. $^{31}P\{^1H\}$ NMR spectra were recorded in either $CDCl_3$ or C_6D_6 at ambient temperature on a Bruker AC250 spectrometer operating at 101.256 MHz; chemical shifts were measured relative to external 85% H_3PO_4. ^{19}F NMR spectra were recorded on the same instrument at 235.36 MHz; chemical shifts were measured relative to external $CFCl_3$. Mass spectra were recorded on a VG7070E instrument by Dr. M. Jones or Miss L. Turner. Elemental analyses were obtained by the microanalytical services of the Chemistry Department, University of Durham.

Synthesis of Ar*P=PAr* **5**

This known diphosphene **5** [1] was prepared via dechlorination of Ar^*PCl_2 by $W(PMe_3)_6$.[15] $W(PMe_3)_6$ (0.500 g, 0.78 mmol) and Ar^*PCl_2 (0.520 g, 1.5 mmol) were placed in an ampoule, and benzene (30 ml) was condensed into the vessel at -196 °C; the reaction mixture was then allowed to warm to room temperature (RT) under vacuum. The mixture was stirred at RT for 36 h. During this time the solution changed colour from yellow/gold to orange. $^{31}P\{^1H\}$ solution-state NMR spectroscopy indicated that the reaction had reached completion, and all of the Ar^*PCl_2 had been consumed. The solution was transferred to a Schlenk vessel and the benzene was removed *in vacuo.* The residue was extracted with n-pentane (3 x 15 ml). The solution was reduced in volume to *ca.* 20 ml, and cooled to -78 °C to give a bright orange crystalline product. It was identified by its characteristic ^{31}P NMR shift (δ 494 ppm).

Synthesis of $Ar^*P=PAr^F$ **1**

This new unsymmetrical diphosphene was similarly prepared. $W(PMe_3)_6$ (0.300 g, 0.46 mmol), Ar^*PCl_2 (0.156 g, 0.45 mmol) and Ar^FPCl_2 (0.175 g, 0.46 mmol) were placed in an ampoule and benzene (30 ml) was condensed into the vessel at -196 °C. The reaction mixture was allowed to warm to RT under vacuum. This mixture was stirred at RT for 36 h, during which time the solution changed colour from yellow/gold to bright red, with some precipitation of a pale solid. After this time ^{31}P NMR indicated that the reaction had reached completion.

The solution was filtered and benzaldehyde (5 ml, 5.22 g, 49 mmol) [10]was added to the filtrate. The mixture was stirred at RT for 48 h, during which time much pale solid precipitated; ^{31}P NMR indicated that this solid contained no diphosphene. After further filtration, Et_2O (15 ml) was added and the solution cooled to 4 °C for 48 h. Further solid precipitated and was filtered off. The benzene and Et_2O were removed *in vacuo.* ^{31}P NMR of the resultant orange oil indicated that the diphosphene was *ca*. 90 % pure. The residue was passed down a silica column using CH_2Cl_2 as eluant. Removal of the solvent *in vacuo* afforded the pure diphosphene **1** as an orange oil. After standing at room temperature for a few days, small florets were observed to crystallise, but these were unsuitable for X-ray diffraction. (Yield 185 mg, 70 %)

Found: C, 55.12, H, 5.30 %; $C_{27}H_{31}F_9P_2$ requires C, 55.11, H, 5.31 %. M/Z 588 [M^+], 307 [M^+ - Ar^F], $^{31}P\{^1H\}$ NMR ($CDCl_3$) 536 (d, Ar*P, $^1J_{PP}$ 570 Hz), 417 (doublet of septets, Ar^FP, $^1J_{PP}$ 570 Hz, $^4J_{PF}$ 22 Hz). ^{19}F NMR (C_6D_6) -56.8 (t, 6F, *o*-CF_3, $^4J_{PF}$ 20 Hz), -63.7 (s, 3F, *p*-CF_3).

Synthesis of Ar'P=PAr^F **7**

As indicated above, this unsymmetrical diphosphene was prepared in two different ways

(a) From Ar^FPCl_2 and Ar'PH_2

DBU (1.44 ml, 9.65 mmol) in THF (15 ml) was added dropwise over 5 min. to a stirred solution of Ar'PH_2 (1.18 g, 4.80 mmol) and Ar^FPCl_2 (1.84 g, 4.80 mmol) in THF (45 ml) at 0 °C. The solution turned brown-yellow, with formation of a precipitate. This mixture was stirred for 30 min after being allowed to warm to RT. The solid was removed by filtration and the filtrate was concentrated to yield a pale yellow powder (1.9 g, 3.4 mmol, crude yield 71%). This solid was washed with several 10 ml aliquots of Et_2O to yield a pure white solid (1.2 g, 2.2 mmol, 46%). Recrystallisation from CH_2Cl_2 (10 ml) gave small crystals unsuitable for X-ray diffraction.

(b) From Ar^FPH_2 and Ar'PCl_2

A similar reaction between DBU (1.90 ml, 12.7 mmol), Ar^FPH_2 (1.97 g, 6.3 mmol) and Ar'PCl_2 (1.98 g, 6.3 mmol) in THF (100 ml) yielded 1.64 g (2.9 mmol, 46%) of the same product **7** after work-up. The ripple tank oscillation technique was employed between 10 and -30 °C for several days in an attempt to obtain better crystals of the diphosphene (0.9 g) in toluene (7 ml), but again only very small crystals resulted. M. Pt. 131 °C. Found, C, 36.33, H, 0.60 %; $C_{17}H_5F_{15}P_2$ requires C, 36.71, H, 0.91 %. M/Z 343 [M^+ - Ar'], 324 [M^+ - Ar' –F], $^{31}P\{^1H\}$ NMR ($CDCl_3$) 489 (d, $^1J_{PP}$ 552 Hz), 478 (d, $^1J_{PP}$ 552 Hz). ^{19}F NMR ($CDCl_3$) *ca*. -53 (12F, *o*-CF_3, complex region with two overlapping doublets of doublets), -64.1 (s, 3F, *p*-CF_3).

Representative synthesis of a platinum complex – Synthesis of *cis*-[$PtCl_2$(PEt_3)(Ar^FP=PAr')] **8**

The platinum dimer *trans*-[$Pt(PEt_3)Cl_2]_2$ (0.58 g, 0.75 mmol) was added to a stirred solution of **7** (0.85 g, 1.5 mmol) in CH_2Cl_2 at room temperature. The mixture was

stirred for 1 h, then cooled to -40° C. The η^1 *cis*-complex **8** was isolated as small transparent crystals, which proved to be unsuitable for X-ray crystallography. Yield 0.62 g (43 %).

Computational Details

All computations were carried out with the Gaussian 09 package.[27] The geometries of compounds listed in Table 2 and the model systems **11**-**22** were fully optimised with the B3LYP functional[28] with no symmetry constraints using the 6-31G* basis set [29] for all atoms apart from Au and Pt, where LANL2DZ pseudopotentials[30] were employed. The much larger 6-311G** and cc-pVDZ basis sets did not show more accurate data (Table S1) compared with results from the 6-31G* basis set and experimental data, thus the 6-31G* basis set is used here for all computations. The polarised continuum solvation model (PCM) with $\varepsilon = 35.7$ was applied in all cases to reflect solvent effects.[31] Calculated ^{31}P NMR chemical shifts at the GIAO-B3LYP/6-31G* level were obtained for the optimised geometries using the $\delta(^{31}P) = 300.0 - 0.9\sigma(^{31}P)$ scale.[32]

Acknowledgements

We thank the EPSRC for financial support, Johnson-Matthey plc for the generous loan of platinum compounds, and Professor M. Yoshifuji for a gift of Ar*PCl_2.

Supporting Information

Table of bond lengths of optimised geometries for selected diphosphenes obtained at 6-31G*, 6-311G** and cc-pVDZ basis sets.

References

[1] (a) M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu, T. Higuchi, J. Am. Chem. Soc. 103 (1981) 4587; (b) M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu, T. Higuchi, J. Am. Chem. Soc. 104 (1982) 6167.

[2] (a) M. Yoshifuji, K. Shibayama, N. Inamoto, T. Matsushita, K. Nishimoto, J. Am. Chem. Soc. 105 (1983) 2495; (b) L. Weber, Chem. Rev. 92 (1992) 1839.

[3] K.B.Dillon, F. Mathey, J. F. Nixon, in 'Phosphorus: the Carbon Copy', Wiley, Chichester, UK, (1998).

[4] M. Scholz, H.W. Roesky, D. Stalke, K. Keller, F.T. Edelmann, J. Organomet. Chem. 366 (1989) 73.

[5] K. B. Dillon, H. P. Goodwin, J. Organomet. Chem. 429 (1992) 169.

[6] K. B. Dillon, V. C. Gibson, J. A. K. Howard, L. J. Sequeira, J. W. Yao, Polyhedron 15 (1996) 4173.

[7] D. V. Partyka, M. P. Washington, T. G. Gray, J. B. Updedraff III, J. F. Turner II , J. D. Protasiewicz, J. Am. Chem. Soc. 131 (2009) 10041.

[8] A. H. Cowley, J. E. Kilduff, J. G. Lasch, N. C. Norman, M. Pakulski, F. Ando, T. C. Wright, J. Am. Chem. Soc. 105 (1983) 7751.

[9] M. Yoshifuji, T. Hashida, N. Inamoto, K. Hirotsu, T. Horiuchi, T. Higuchi, K. Ito, S. Nagase, Angew. Chem. Int. Ed. 24 (1985) 211.

[10] I. Kovacs, H. Krautscheid, E. Matern, G. Fritz, Z. Anorg. Allg. Chem. 623 (1997) 1088.

[11] H. Krautscheid, E. Matern, J. Olkowska-Oetzel, J. Pikies, G. Fritz, Z. Anorg. Allg. Chem. 627 (2001) 675.

[12] E. Baum, E. Matern, A. Robaszkiewicz, J. Pikies, Z. Anorg. Allg. Chem. 632 (2006) 1073.

[13] W. Domańska-Babul, J. Chojnacki, E. Matern, J. Pikies, J. Organomet. Chem. 692 (2007) 3640.

[14] M. Demange, X.-F. Le Goff, P. Le Floch, N. Mézailles, Chem. Eur. J. 16 (2010) 12064.

[15] K. B. Dillon, V. C. Gibson, L. J. Sequeira, J. Chem. Soc., Chem. Commun. (1995) 2429.

[16] (a) K. B. Dillon, H. P. Goodwin, J. Organomet. Chem. 469 (1994) 125; (b) H. Eshtiagh-Hosseini, H. W. Kroto, J. F. Nixon, M. J. Maah, M. J. Taylor. J. Chem. Soc., Chem. Commun. (1981) 199.

[17] S. Berger, S. Braun, H.-O. Kalinowski, 'NMR Spectroscopy of the Non-Metallic Elements', Wiley, Chichester (1997).

[18] M. J. Atherton, J. Fawcett, J. H. Holloway, E. G. Hope, D. R. Russell, G. C. Saunders, J. Chem. Soc Dalton Trans. (1997) 2217.

[19] C. Corcoran, J. Fawcett, S. Friedrichs, J. H. Holloway, E. G. Hope, D. R. Russell, G. C. Saunders, A. M. Stuart, J. Chem. Soc. Dalton Trans. (2000) 161.

[20] E. M. Pelczar, E. A. Nytko, M. A. Zhuravel, J. M. Smith, D. S. Glueck, R. Sommer, C. D. Incarvito, A. L. Rheingold, Polyhedron 21 (2002) 2409.

[21] A.H. Cowley, A. Decken, N.C. Norman, C. Kruger, F. Lutz, H. Jacobsen, T. Ziegler, J. Am. Chem. Soc. 119 (1997) 3389.

[22] T. Lübben, H.W. Roesky, H. Gornitzka, A. Steiner, D. Stalke, Eur. J. Solid State Inorg. Chem. 32 (1995) 121.

[23] A. Dubourg, J.-P. Declercq, H. Ranaivonjatovo, J. Escudié, C. Couret, M. Lazraq, Acta Cryst. C 44 (1988) 2004.

[24] J. Escudié, C. Couret, H. Ranaivonjatovo, M. Lazraq, J. Satge, Phosphorus and Sulfur 31 (1987) 27.

[25] S. Loss, C. Widauer, H. Grützmacher, Angew. Chem. Int. Ed. 38 (1999) 3329.

[26] L. Weber, H. Schumann, R. Boese, Chem. Ber. 123 (1990) 1779.

[27] Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, Jr., J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, (2009).

[28] (a) A. D. Becke, J. Chem. Phys. 98 (1993) 5648; (b) C. Lee, W. Yang, R. G. Parr, Phys. Rev. B 37 (1988) 785.

[29] (a) G. A. Petersson, M. A. Al-Laham, J. Chem. Phys. 94 (1991) 6081; (b) G. A. Petersson, A. Bennett, T. G. Tensfeldt, M. A. Al-Laham, W. A. Shirley, J. Mantzaris, J. Chem. Phys. 89 (1988) 2193.

[30] (a) T. H. Dunning Jr., P. J. Hay, Modern Theoretical Chemistry, Ed. H. F. Schaefer III, Vol. 3 Plenum, New York, (1976) (b) P. J. Hay, W. R. Wadt, J. Chem. Phys. 82 (1985) 270; (c) W. R. Wadt, P. J. Hay, J. Chem. Phys. 82 (1985) 284; (d) P. J. Hay, W. R. Wadt, J. Chem. Phys. 82 (1985) 299.

[31] J. N. Harvey, K. M. Heslop, A. G. Orpen, P. G. Pringle, Chem. Commun. (2003) 278.

[32] (a) R. Ditchfield, Mol. Phys. 27 (1974) 789; (b) C. M. Rohling, L. C. Allen, R. Ditchfield, Chem. Phys. 87 (1984) 9; (c) K. Wolinski, J. F. Hinton, P. Pulay, J. Am. Chem. Soc. 112 (1990) 8251.

Highlights

- some new unsymmetrical diphosphenes and their platinum(II) complexes synthesised
- configurations assigned by a combination of ^{31}P solution-state NMR and high-level theoretical calculations
- steric and electronic effects both important influences on the configuration adopted